

PATENT APPLICATION TRANSMITTAL LETTER

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Washington, D.C. 20231

Transmitted herewith for filing is the patent application of:_____

Tsuquo KOYANAGI and Hiroyasu NISHIDA

Entitled: "INORGANIC COMPOUND SOL MODIFIED BY ORGANIC COMPOUND"

Enclosed is a:

- sheet(s) of drawing(s)
- X An Assignment of the invention to:
 CATALYSTS & CHEMICALS INDUSTRIES CO., LTD.
- X Declaration and Power of Attorney
- X Verified Statement Claiming Small Entity Status
- X Preliminary Amendment
- X Claim for Priority and certified copy

CLAIMS AS FILED

| | <u>No. Filed</u> | <u>No. Extra</u> | | <u>Small Entity Rate</u> | <u>Non-Small Entity Rate</u> | <u>Charge</u> |
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| Multiple Dependent Claim/s | | | | \$135.00 | \$270.00 | \$ <u> 0 </u> |
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An original and two copies of this sheet are enclosed.

March 11, 1998
Date

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PATENT APPLICATION

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re application of :
TSUGUO KOYANAGI and : INORGANIC COMPOUND SOL
HIROYASU NISHIDA : MODIFIED BY ORGANIC
: COMPOUND
Serial No. Not Yet Assigned :
Filed Concurrently Herewith :

Pittsburgh, Pennsylvania
March 11, 1998

PRELIMINARY AMENDMENT

Box PATENT APPLICATION
Assistant Commissioner for Patents
Washington D.C. 20231

Sir:

Prior to initial examination, please amend the above-identified patent application as follows:

IN THE SPECIFICATION:

Page 2, line 24, delete "the" and insert --a--.

Page 2, line 26, delete "the" and insert --its--.

Page 3, line 3, delete "the".

Page 3, line 4, delete "the" and insert --a--.

Page 3, line 5, delete "a" and insert --the--.

Page 3, line 6, delete "turns to be" and insert therefor --becomes--.

Page 3, line 8, delete "for" and insert --used in--.

Page 3, line 8, after "forming" insert --process--.

Page 3, line 11, delete "etc." and insert --and the like--.

Page 3, line 13, before "dispersibility" delete "the".

Page 3, line 15, delete "the".

Page 3, line 16, delete "the".

Page 3, line 17, delete "to obtain" and insert --as--.

Page 3, line 18, after "in" delete "the".

Page 3, line 23, delete "OBJECT OF THE INVENTION".

Page 3, line 25, after "and" delete "the" and insert --an--.

Page 5, line 11, delete "be composite oxide particulates".

Page 11, line 13, after "agent" insert --and--.

Page 11, line 14, after "present" insert --in the--.

Page 11, line 16, after "from" insert --a--.

Page 11, line 20, after "also" insert --in--.

Page 11, line 22, after "or" insert --as--.

Page 12, line 10, delete "[Preparation of surface-modified sol]" and insert --(a) Preparation of surface-modified sol--.

Page 13, line 3, delete "[Evaluation of sol stability I]" and insert --(b) Evaluation of sol stability I--.

Page 13, line 10, delete "[Evaluation of sol stability II]" and insert --(c) Evaluation of sol stability II--.

Page 13, line 18, delete "[Evaluation of sol stability III]" and insert --(d) Evaluation of sol stability III--.

Page 18, line 25, delete "[Preparation of surface-modified sol]" and insert --(a) Preparation of surface-modified sol--.

Page 19, line 20, delete "[Evaluation of sol stability IV]" and insert --(b) Evaluation of sol stability IV--.

Page 20, line 1, delete "[Evaluation of sol stability V]" and insert --(c) Evaluation of sol stability V--.

IN THE ABSTRACT:

Page 28, line 2, delete "The" and insert --An--.

Page 28, line 2, delete "of the present invention".

Page 28, line 7, delete "This" and insert --The--.

Page 28, line 8, delete "has" and insert --possesses a--.

Page 28, line 8, before "dispersion" insert --the--.

Page 28, line 8, delete "so that its" and insert therefor --providing excellent--.

Page 28, line 9, delete "is excellent without" and insert --while avoiding--.

REMARKS

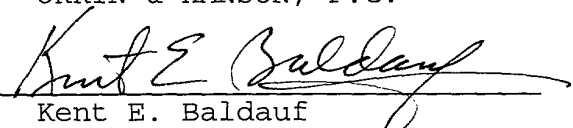
The specification and Abstract have been amended to place them in conformance with standard United States patent practice.

Examination and allowance of pending claims 1-4 are respectfully requested.

Respectfully submitted,

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Applicant or Patentee: Hiroyasu NISHIDA Attorney's
Serial or Patent No.: _____ Docket No.: _____
Filed or Issued: _____
For: INORGANIC COMPOUND SOL MODIFIED BY ORGANIC COMPOUND

I hereby declare that I am

I hereby declare that the above identified small business concern qualifies as a small business concern as defined in 13 CFR 121.12, and reproduced in 37 CFR 1.9(d), for purposes of paying reduced fees to the United States Patent and Trademark Office, in that the number of employees of the concern, including those of its affiliates, does not exceed 500 persons. For purposes of this statement, (1) the number of employees of the business concern is the average over the previous fiscal year of the concern of the persons employed on a full-time, part-time or temporary basis during each of the pay periods of the fiscal year, and (2) concerns are affiliates of each other when either, directly or indirectly, one concern controls or has the power to control the other, or a third party or parties controls or has the power to control both.

I hereby declare that rights under contract or law have been conveyed to and remain with the small business concern identified above with regard to the invention, entitled INORGANIC COMPOUND SOL MODIFIED BY ORGANIC COMPOUND by inventor(s) Tsuquo KOYANAGI and Hiroyasu NISHIDA described in

 X the specification filed herewith.
 application serial no. _____, filed _____
 patent no. _____, issued _____

If the rights held by the above identified small business concern are not exclusive, each individual, concern or organization having rights in the invention is listed below* and no rights to the invention are held by any person, other than the inventor, who would not qualify as an independent inventor under 37 CFR 1.9(c) if that person made the invention, or by any concern which would not qualify as a small business concern under 37 CFR 1.9(d), or a nonprofit organization under 37 CFR 1.9(e). *NOTE: Separate verified statements are required from each named person, concern or organization having rights to the invention averring to their status as small entities. (37 CFR 1.27)

| | | | |
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I acknowledge the duty to file, in this application or patent, notification of any change in status resulting in loss of entitlement to small entity status prior to paying, or at the time of paying, the earliest of the issue fee or any maintenance fee due after the date on which status as a small entity is no longer appropriate. {37 CFR 1.28(b)}

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under section 1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the application, any patent issuing thereon, or any patent to which this verified statement is directed.

NAME OF PERSON SIGNING Osamu UTSUMI

TITLE OF PERSON IF OTHER THAN OWNER Representative

ADDRESS OF PERSON SIGNING C/O CATALYSTS & CHEMICALS INDUSTRIES CO., LTD.

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SIGNATURE

Osamu Utsumi

DATE

February 25, 1998

Kanagawa 210-0913,
Japan

TITLE

INORGANIC COMPOUND SOL MODIFIED BY ORGANIC COMPOUND

FIELD OF THE INVENTION

5 The present invention relates to an inorganic compound
sol having inorganic compound particulates dispersed in a
dispersion media, which inorganic compound sol can be used
in a coating material, a hard coating agent, an insulating
coat and a protective coat of electrical and electronic
10 part, an additional agent of cement, and a binder of
inorganic fiber, etc. More particularly, the present
invention is concerned with an inorganic compound sol in
which the surface of inorganic compound particulates is
modified by a specified organic compound to thereby exhibit
15 excellent dispersion stability in dispersion media.

BACKGROUND OF THE INVENTION

 Particulates of an inorganic oxide such as silica or
alumina must generally have their surface rendered
20 hydrophobic for obtaining an organic solvent dispersion
thereof. Thus, generally, the surface of such particulates
is modified.

 A method of modifying the surface of such inorganic
compound particulates comprises reacting, for example, a
25 reactive monomer or a coupling agent with hydroxyl groups
of the particulate surface. This method is carried out,
for example, by dispersing powdery particulates in an
organic solvent and adding a modifier to the dispersion to

thereby modify the particulate surface, or by conducting a solvent substitution so as to replace water of an aqueous dispersion of particulates by an organic solvent and adding a modifier to the dispersion to thereby modify the
5 particulate surface.

However, these methods cannot completely inhibit the aggregation of particulates, thereby rendering it difficult to obtain an organic solvent sol of high dispersibility.

Moreover, the problem has been encountered such that,
10 when the above inorganic compound particulates are used as a filler in, for example, a coating material, a hard coating agent component of an insulting coat and a protective coat, adding a sol thereof to a matrix of coating film forming agent is likely to invite an
15 aggregation of particulates in the matrix. Especially, the defect has been encountered such that, when the organic solvent sol is used in the presence of cation, anion, or surfactant, particulates may be aggregated and a gelation may occur.

20 For example, for the use for the coating material, in order to improve the hardness, water resistance and stain resistance of the coating films, an organic solvent sol in which the inorganic compound particulates had been dispersed has been used. However, the problem has been
25 encountered such that the coating material becomes viscous and whitens since such organic solvent sol is poor in the compatibility with the coating film-formed resin and the resin emulsion being obtained.

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Further, for the hard coating agent, in order to improve properties of the film being formed, such as the hardness and water resistance, the inorganic compound particulates have been used as fillers. However, the problem has been encountered such that a hard coating film being formed turns to be opaque since the particulates are poor in the dispersing stability in the coating solution for the coating film forming. Also in the case that such organic solvent sol is used as a solution for an insulating film and a protective film forming for electrical and electronic components, etc., the problem has been encountered such that the coating solution becomes viscous since the particulates are poor in the dispersibility in the coating solution.

Furthermore, in order to improve the soil strength, a sol in which the inorganic compound particulates had been dispersed has been added to a cement to obtain a soil stabilizer. In the event that the sol is poor in the stability, the problem has been encountered that it has been hard to fill up crevices between the soils and moles with the inorganic compound particulates.

OBJECT OF THE INVENTION

The present invention has been made in view of the above circumstances, and the object of the present invention is to provide an inorganic compound sol modified by an organic compound, which is excellent in dispersion stability.

SUMMARY OF THE INVENTION

The inorganic compound sol of the present invention comprises a dispersion medium and, dispersed therein,
5 inorganic compound particulates whose surface has been modified by an organic compound exhibiting a molecular polarizability of from 2×10^{-40} to $850 \times 10^{-40} \text{ C}^2\text{m}^2\text{J}^{-1}$.

It is preferred that the inorganic compound particulates are silica particulates, or composite oxide
10 particulates composed of silica and at least one inorganic oxide other than silica.

Further, the above dispersion medium preferably has a dielectric constant of from 10 to 85.

15

DETAILED DESCRIPTION OF THE INVENTION

The present invention will be described in greater detail below.

The inorganic compound sol of the present invention comprises a dispersion medium and, dispersed therein,
20 inorganic compound particulates whose surface has been modified by an organic compound exhibiting a molecular polarizability of from 2×10^{-40} to $850 \times 10^{-40} \text{ C}^2\text{m}^2\text{J}^{-1}$.

The terminology "molecular polarizability" used herein defines the magnitude of dipole moment which is produced by
25 a shift of negatively charged electron cloud of a molecule from the positively charged nucleus by the action of external electric field surrounding the molecule. The molecular polarizability is expressed by the formula:

$$\alpha_0 = 4\pi\epsilon_0 R^3 \quad (\text{C}^2\text{m}^2\text{J}^{-1})$$

wherein α_0 represents the molecular polarizability, ϵ_0 represents the dielectric constant, and R represents the molecular radius.

5

Inorganic compound particulates

Examples of the inorganic compound particulates suitably employed in the present invention include particulates of silica, alumina, titania, zirconia and other inorganic oxides or composite oxides of these. Of
 10 the above particulates, silica particulates or composite oxides be composite oxide particulates composed of silica and at least one inorganic oxide other than silica such as silica/alumina and silica/zirconia are preferred. The above silica particulates can be produced by, for example,
 15 the process described in the applicant's prior applications published as Japanese Patent Publication Nos. 4(1992)-56775 and 4(1992)-55125.

Examples of the inorganic oxides other than silica include oxides of elements selected from among those of
 20 Group 1A, Group 2A, Group 2B, Group 3A, Group 3B, Group 4A, Group 4B, Group 5A, Group 5B and Group 6A of the periodic table. Specific examples thereof include Li_2O , Na_2O , K_2O , Rb_2O , BeO , MgO , CaO , ZnO , Y_2O_3 , La_2O_3 , Al_2O_3 , Ga_2O_3 , B_2O_3 , Ce_2O_3 , Sb_2O_3 , P_2O_5 , TiO_2 , ZrO_2 , SnO_2 , MoO_3 and WO_3 .

25 The above silica containing composite oxides can be produced by, for example, the process described in the applicant's prior applications published as Japanese Patent

Laid-open Publication Nos. 5(1993)-132309 and 7(1995)-10522.

For example, the silica containing composite oxides can be produced by simultaneously adding an alkali metal silicate, such as sodium silicate, and an alkali soluble inorganic compound to an alkali aqueous solution having a pH value of at least 10 and reacting them without controlling the pH concentration of the reaction mixture.

Alternatively, the silica containing composite oxides can be produced by dispersing seed particulates composed of particulates of silica, alumina and other inorganic oxides in an alkali aqueous solution having a pH value of at least 10 and adding the above silicate and alkali soluble inorganic compound to the dispersion so that the particulates grow.

In the silica containing composite oxide particulates, the weight ratio of silica to inorganic oxides other than silica (SiO_2 /other inorganic oxides) preferably ranges from 0.1 to 500 and, still preferably, from 5 to 300.

The size of inorganic compound particulates for use in the present invention is not particularly limited as long as the sol containing the inorganic compound particulates is stable.

These inorganic compound particulates are preferably contained in the inorganic compound sol in an amount of from 1 to 50% by weight, still preferably, from 5 to 30% by weight.

Organic compound

In the inorganic compound sol of the present invention, the surface of the above inorganic oxide is modified by an organic compound exhibiting a molecular polarizability of from 2×10^{-40} to $850 \times 10^{-40} \text{ C}^2\text{m}^2\text{J}^{-1}$,
 5 preferably, from 5×10^{-40} to $850 \times 10^{-40} \text{ C}^2\text{m}^2\text{J}^{-1}$.

Examples of the organic compounds exhibiting the above molecular polarizability include:

- vinylsilane compounds such as vinyltrimethoxysilane, vinyltriethoxysilane, vinylmethyldimethoxysilane,
 10 vinylmethyldiethoxysilane and vinylphenyldimethoxysilane;
 acrylsilane compounds such as γ -acryloxypropyltrimethoxysilane, γ -acryloxypropylphenyldimethoxysilane, γ -methacryloxypropyltrimethoxysilane and γ -
 15 methacryloxypropylphenyldimethoxysilane;
 epoxysilane compounds such as γ -glycidoxypropyltrimethoxysilane and γ -glycidoxypropylmethyldiethoxysilane;
 aminosilane compounds such as γ -
 20 aminopropyltriethoxysilane; and
 γ -mercaptopropyltrimethoxysilane and γ -chloropropyltrimethoxysilane.

Also, use can be made of a reactive monomer such as styrene monomer or an acrylic acid monomer, e.g., ethyl
 25 methacrylate. Further, use can be made of a linear alcohol such as butanol.

The reactive monomer may polymerize at the stage of modification, so that at least part thereof becomes a polymer.

The above organic compounds may be used either
5 individually or in combination.

When the molecular polarizability of the organic compound is lower than $2 \times 10^{-40} \text{ C}^2\text{m}^2\text{J}^{-1}$, the organic properties of the organic compound are decreased so that the organic compound has low affinity with the organic
10 solvent. Therefore, the particulates whose surface has been modified by this organic compound have poor dispersibility in the organic solvent. In particular, when an acid, a base, a salt, or a surfactant thereof is present in the inorganic compound sol, the particulates are likely
15 to aggregate with each other.

Dispersion media

In the inorganic compound sol of the present invention, preferred use is made of a dispersion medium (solvent) whose dielectric constant is from 10 to 85. When
20 the dielectric constant is less than 10, the particulates are unstable in the sol, so that a gelation may occur.

Examples of such organic solvents include water; monohydric alcohols such as ethanol, propanol and butanol; polyhydric alcohols such as ethylene glycol and propylene
25 glycol; alcohol ethers such as ethylene glycol monoethyl ether; amide solvents such as N-methylformamide, N,N-dimethylformamide and N-methylacetamide; and lactones such as γ -butyrolactone and N-methyl-2-pyrrolidone. These

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dispersion media may be used either individually or in combination. When water is used as a dispersion medium, a dielectric constant of used water is preferably from 60 to 85.

5 An organic or inorganic acid, an organic base or inorganic base, a salt, or a surfactant thereof may be added to these dispersion media. Examples of suitable organic or inorganic acids thereof include hydrochloric acid, sulfuric acid, nitric acid, phosphoric acid, perchloric acid, acetic acid. Examples of suitable organic
10 or inorganic bases thereof include ammonium hydroxide, organic amine, hydroxide of alkali metals or alkali earth metals. Examples of suitable surfactants thereof include sodium alkylbenzenesulfonate, sodium alkylsulfonate.

15 Method of preparing inorganic compound sol

The inorganic compound sol of the present invention can be prepared by the following method.

In the step (a), an organic compound for modifying the surface of inorganic compound particulates is added to a
20 dispersion of inorganic compound particulates.

The dispersion of inorganic compound particulates may be a water dispersion, an organic solvent dispersion, or a dispersion in a mixture of water and an organic solvent. It is preferred that the inorganic compound particulates be
25 contained in the above dispersion in an amount of 0.1 to 50% by weight, especially, 1 to 20% by weight.

The surface modifying organic compound is added preferably in an amount of 0.1×10^{-6} to 50×10^{-6} mol/m²

and, still preferably, 1×10^{-6} to 30×10^{-6} mol/m² in terms of the amount of modification per outer surface area of the inorganic compound particulates dispersed in the dispersion. When the amount is less than 0.1×10^{-6} mol/m², the effect of modification is unsatisfactory. Even when the organic compound is used in amounts greater than 50×10^{-6} mol/m², the effect of modification is no longer enhanced.

In the step (b), after the addition of a specified amount of surface modifying organic compound, the dispersion is heated at 50°C or higher temperatures, preferably, 60°C or higher temperatures.

Thus, the surface of the inorganic compound reacts with the surface modifying organic compound, so that the modification of the surface of the inorganic compound is advanced.

In the step (c), when a dispersion medium (organic solvent) whose dielectric constant is lower than 10 is contained in the surface-modified inorganic compound sol obtained above, a solvent displacement replacing it by dispersion media whose dielectric constant is at least 10 may be carried out.

The solvent displacement may be performed by the use of, for example, an ultrafilter or a rotary evaporator.

EFFECT OF THE INVENTION

In the inorganic compound sol of the present invention, the surface of the inorganic compound

particulates is modified by the organic compound having specified molecular polarizability. Therefore, the inorganic compound particulates have desirable affinity with the dispersion media, so that the dispersion stability thereof in the dispersion media are excellent without the occurrence of aggregation of particulates and gelation. Further, even if an organic or inorganic acid or a salt thereof is present in the inorganic compound sol, the inorganic compound particulates would not aggregate with each other and the gelation would not occur.

When the inorganic compound sol of the present invention is blended as a filler in, for example, a coating material or a hard coating agent even if an acid, base, salt, surfactant, et al. is present inorganic compound sol, the finally obtained coating film is substantially free from transparency decrease and cracking attributed to the aggregation of particulates and the gelation. Therefore, the inorganic compound sol of the present invention is useful as a filler to be blended in not only various coating materials and hard coating agents but also various resins. The inorganic compound sol is suitably employed as, for example, a magnetic tape filler or a film blocking preventive agent.

Further, when the inorganic compound sol of the present invention is added to a cement, excessively quick caking of a cement is retarded because of a low gelation rate. The inorganic compound sol can easily fill up crevices between the soils and moles. The cement is caked

after filling. Therefore, the inorganic compound sol of the present invention is useful as an additive for cement for water stop or soil strength.

5

EXAMPLE

The present invention will now be illustrated in greater detail with reference to the following Examples, which in no way limit the scope of the invention.

Example 1

10

[Preparation of surface-modified sol]

500 g of a silica/alumina water dispersion sol (Catalysts & Chemicals Industries Co., Ltd., Cataloid-SN, weight ratio of $\text{SiO}_2/\text{Al}_2\text{O}_3 = 285.7$, average particle size: 12 nm and solid content: 20% by weight) was used as a starting material and subjected to a solvent displacement by means of an ultrafilter to thereby replace the water by methanol. Thus, there was obtained a methanol dispersion sol having a solid content of 30% by weight.

15

300 g of this sol was mixed with 2700 g of ethanol, and 8.4 g of γ -glycidoxypropyltrimethoxysilane was added to the mixture. The mixture was agitated for 1 hr, thereby obtaining a sol containing silica/alumina particulates whose surface was modified by γ -glycidoxypropyltrimethoxysilane.

20

196 g of ethylene glycol was added to the obtained sol and heated at 60°C for 1 hr. Thereafter, ethanol was removed in vacuum by the use of a rotary evaporator, thereby obtaining a surface-modified silica/alumina sol of

25

30% by weight in solid content which contained ethylene glycol as a dispersion medium.

[Evaluation of sol stability I]

10 parts by weight of each of an aqueous solution of
5 sulfuric acid (2% by weight) and an aqueous solution of
hydrochloric acid (2% by weight) was mixed with 100 parts
by weight of the obtained surface-modified silica/alumina
sol, and the sol stability I was evaluated.

The results are given in Table 1.

10 [Evaluation of sol stability II]

10 parts by weight of an aqueous solution of ammonium
sulfate (5% by weight) was mixed with 100 parts by weight
of the obtained surface-modified silica/alumina sol, and a
mixture was stirred for 10 min. Then the mixture was
15 allowed to stand in a bath kept at 70°C, and the sol
stability II was evaluated.

The results are given in Table 2.

[Evaluation of sol stability III]

10 parts by weight of an aqueous solution of sodium
20 chloride (5% by weight) was mixed with 100 parts by weight
of the obtained surface-modified silica/alumina sol, and a
mixture was stirred for 10 min. Then the mixture was
allowed to stand in a bath kept at 70°C, and the sol
stability III was evaluated.

25 The results are given in Table 3.

Example 2

A surface-modified silica/zirconia sol was obtained in
the same manner as in Example 1, except that a

silica/zirconia water dispersion sol (weight ratio of $\text{SiO}_2/\text{ZrO}_2$: 3, average particle size: 30 nm and solid content: 20% by weight) was used as a starting material.

The sol stability I of the obtained surface-modified
5 silica/zirconia sol was evaluated in the same manner as in Example 1.

The results are given in Table 1.

Example 3

A surface-modified silica/titania sol was obtained in
10 the same manner as in Example 1, except that a silica/titania water dispersion sol (weight ratio of $\text{SiO}_2/\text{TiO}_2$: 9, average particle size: 10 nm and solid content: 20% by weight) was used as a starting material.

The sol stability I of the obtained surface-modified
15 silica/titania sol was evaluated in the same manner as in Example 1.

The results are given in Table 1.

Example 4

A surface-modified composite oxide sol was obtained in
20 the same manner as in Example 1, except that a sol mixture consisting of 250 g of a silica/alumina water dispersion sol (weight ratio of $\text{SiO}_2/\text{Al}_2\text{O}_3$: 285.7, average particle size: 12 nm and solid content: 20% by weight) and 250 g of a silica/zirconia water dispersion sol (weight ratio of
25 $\text{SiO}_2/\text{ZrO}_2$: 3, average particle size: 30 nm and solid content: 20% by weight) was used as a starting material.

The sol stability I of the obtained surface-modified composite oxide sol was evaluated in the same manner as in Example 1.

The results are given in Table 1.

5 Example 5

A surface-modified silica/tin oxide sol was obtained in the same manner as in Example 1, except that a silica/tin oxide water dispersion sol (weight ratio of $\text{SiO}_2/\text{SnO}_2$: 19, average particle size: 10 nm and solid content: 20% by weight) was used as a starting material and that N-methylpyrrolidone was used as a dispersion medium.

The sol stability I of the obtained surface-modified silica/tin oxide sol was evaluated in the same manner as in Example 1.

15 The results are given in Table 1.

Example 6

A surface-modified silica/indium oxide sol was obtained in the same manner as in Example 1, except that a silica/indium oxide water dispersion sol (weight ratio of $\text{SiO}_2/\text{In}_2\text{O}_3$: 5.7, average particle size: 11 nm and solid content: 20% by weight) was used as a starting material and that γ -butyrolactone was used as a dispersion medium.

25 The sol stability I of the obtained surface-modified silica/indium oxide sol was evaluated in the same manner as in Example 1.

The results are given in Table 1.

Example 7

A surface-modified silica/alumina sol was obtained in the same manner as in Example 1, except that 5.0 g of vinyltrimethoxysilane was used in place of 8.4 g of γ -glycidoxypropyltrimethoxysilane.

- 5 The sol stability I of the obtained surface-modified silica/alumina sol was evaluated in the same manner as in Example 1.

The results are given in Table 1.

Example 8

- 10 A surface-modified silica/antimony oxide sol was obtained in the same manner as in Example 1, except that a silica/antimony water dispersion sol (weight ratio of $\text{SiO}_2/\text{Sb}_2\text{O}_5$: 5.7, average particle size: 15 nm and solid content: 20% by weight) was used as a starting material.

- 15 The sol stability I of the obtained surface-modified silica/antimony oxide sol was evaluated in the same manner as in Example 1.

The results are given in Table 1.

Example 9

- 20 A surface-modified silica/tungsten oxide sol was obtained in the same manner as in Example 1, except that a silica/tungsten oxide water dispersion sol (weight ratio of SiO_2/WO_3 : 4, average particle size: 16 nm and solid content: 20% by weight) was used as a starting material, that 9.0 g
25 of γ -methacryloxypropyl-trimethoxysilane was used in place of 8.4 g of γ -glycidoxypropyltrimethoxysilane and that methyl cellosolve was used in place of ethylene glycol as a dispersion medium.

The sol stability I of the obtained surface-modified silica/tungsten oxide sol was evaluated in the same manner as in Example 1.

The results are given in Table 1.

5 Example 10

The methanol-dispersed silica/alumina sol of 30% by weight in solid content which was obtained in Example 1 was diluted with methanol to a solid content of 5% by weight. 8 g of 2,2'-azobis(2-aminodipropene) dihydrochloride was added to 1000 g of the resultant sol and, further, 30 g of styrene monomer was mixed thereinto, followed by agitation at 85°C for 5 hr. Thus, there was obtained a sol comprising silica/alumina particulates whose surface was modified by polystyrene.

15 450 g of ethylene glycol was added to the obtained sol and the obtained sol was heated at 60°C for 1 hr. Thereafter, alcohol was removed in vacuum by the use of a rotary evaporator, thereby obtaining a surface-modified silica/alumina sol of 10% by weight in solid content which
20 contained ethylene glycol as a dispersion medium.

The sol stability I of the obtained surface-modified silica/alumina sol was evaluated in the same manner as in Example 1.

The results are given in Table 1.

25 Example 11

A surface-modified silica/alumina sol was obtained in the same manner as in Example 10, except that methyl methacrylate was used in place of styrene.

The sol stability I of the obtained surface-modified silica/alumina sol was evaluated in the same manner as in Example 1.

The results are given in Table 1.

5 Example 12

340 g of n-butanol was added to 300 g of the methanol-dispersed sol of silica/alumina composite oxide (solid content: 20% by weight) prepared by the same solvent substitution as in Example 1, and a solvent displacement
10 was carried out in vacuum. Thus, there was obtained 400 g of a sol of silica/alumina dispersed in n-butanol. This sol was heated at 150°C for 3 hr in an autoclave.

240 g of ethylene glycol was added to the obtained sol and heated at 60°C for 1 hr. Thereafter, n-butanol was
15 removed in vacuum by the use of a rotary evaporator, thereby obtaining a sol of silica/alumina whose surface was modified by n-butanol, which had a solid content of 20% by weight and which contained ethylene glycol as a dispersion medium.

20 The sol stability I of the obtained surface-modified silica/alumina sol was evaluated in the same manner as in Example 1.

The results are given in Table 1.

Example 13

25

[Preparation of surface-modified sol]

330 g of a silica water dispersion sol (Catalysts & Chemicals Industries Co., Ltd., Cataloid-SI-30, average particle size: 12 nm and solid content: 30% by weight) as a

starting material was mixed with 170g of water and 50 g of cation-exchange resin, and followed by agitation for 30 min.

The cation-exchange resin separated from the mixture, and then 6.7 g of γ -glycidoxypopyltrimethoxysilane was added to 400 g of the obtained silica sol having pH value of 4. The mixture was agitated for 1 hr at 60°C, thereby obtaining a sol containing silica/alumina particulates whose surface was modified by γ -glycidoxypopyltrimethoxysilane.

Thereafter, the sol containing silica particulates was concentrated in vacuum by the use of a rotary evaporator, thereby obtaining a surface-modified silica sol of 30% by weight in solid content which contained water as a dispersion medium.

The sol stability II and III of the obtained surface modified silica sol was evaluated in the same manner as in Example 1.

The results are given in Table 2 and 3.

[Evaluation of sol stability IV]

A mixed solution (A) which was mixed 100 parts by weight of the obtained surface-modified silica sol and 100 parts by weight of water and the other mixed solution (B) which was mixed 250 parts by weight of a portland cement and 420 parts by weight of water mixed and kept at 30°C. Then the time taken until the mixture cemented was measured as the evaluation of sol stability IV.

The results are given in Table 4.

[Evaluation of sol stability V]

100 parts by weight of an acrylic resin emulsion produced by Union Paint Company which was dispersion having pH value of 9 of an acrylic resin of 50% by weight in aqueous solution containing surfactant was mixed with 100 parts by weight of the obtained surface-modified silica sol, and a mixture was stirred for 10 min. Then the mixture was allowed to stand in a bath kept at 70°C, and the sol stability was evaluated.

10 The results are given in Table 5.

Comparative Example 1

A silica/alumina sol containing ethylene glycol as a dispersion medium was obtained from the silica/alumina water dispersion sol of Example 1 in the same manner as in Example 1, except that any modification using an organic compound was not performed.

The sol stability I of the obtained silica/alumina sol was evaluated in the same manner as in Example 1.

The results are given in Table 1.

20 Comparative Example 2

A silica/alumina sol was obtained in the same manner as in Example 1, except that 4 g of monomethyltrimethoxysilane was used in place of 8.4 g of γ -glycidoxypropyltrimethoxysilane.

25 The sol stability I of the obtained silica/alumina sol was evaluated in the same manner as in Example 1.

The results are given in Table 1.

Comparative Example 3

A silica/zirconia sol was obtained from the silica/zirconia water dispersion sol (weight ratio of $\text{SiO}_2/\text{ZrO}_2$: 3, average particle size: 30 nm and solid content: 20% by weight) of Example 2 in the same manner as
5 in Example 2, except that any surface modification using an organic compound was not performed and that N-methylpyrrolidone was used as a dispersion medium.

The sol stability I of the obtained silica/zirconia sol was evaluated in the same manner as in Example 1.

10 The results are given in Table 1.

Comparative Example 4

The sol stability II, III, IV and V of a silica water dispersion sol (Catalysts & Chemicals Industries Co., Ltd., Cataloid-SI-30, average particle size: 12 nm and solid
15 content: 30% by weight) was evaluated in the same manner as in Example 13.

The results are given in Table 2 to 5.

Table 1

| | Sol composition | Modifying organic compound | |
|-------------|---|--|------------------------|
| | | | mol. polarizability |
| Ex. 1 | $\text{SiO}_2 \cdot \text{Al}_2\text{O}_3$ | γ -glycidoxypentyl trimethoxysilane | 10.4×10^{-40} |
| Ex. 2 | $\text{SiO}_2 \cdot \text{ZrO}_2$ | γ -glycidoxypentyl trimethoxysilane | 10.4×10^{-40} |
| Ex. 3 | $\text{SiO}_2 \cdot \text{TiO}_2$ | γ -glycidoxypentyl trimethoxysilane | 10.4×10^{-40} |
| Ex. 4 | $\text{SiO}_2 \cdot \text{Al}_2\text{O}_3$ + $\text{SiO}_2 \cdot \text{ZrO}_2$ | γ -glycidoxypentyl trimethoxysilane | 10.4×10^{-40} |
| Ex. 5 | $\text{SiO}_2 \cdot \text{SnO}_2$ | γ -glycidoxypentyl trimethoxysilane | 10.4×10^{-40} |
| Ex. 6 | $\text{SiO}_2 \cdot \text{In}_2\text{O}_3$ | γ -glycidoxypentyl trimethoxysilane | 10.4×10^{-40} |
| Ex. 7 | $\text{SiO}_2 \cdot \text{Al}_2\text{O}_3$ | vinyltrimethoxy silane | 4.0×10^{-40} |
| Ex. 8 | $\text{SiO}_2 \cdot \text{Sb}_2\text{O}_5$ | vinyltrimethoxy silane | 4.0×10^{-40} |
| Ex. 9 | $\text{SiO}_2 \cdot \text{WO}_3$ | γ -methacryloxy propyltrimethoxy silane | 12.7×10^{-40} |
| Ex. 10 | $\text{SiO}_2 \cdot \text{Al}_2\text{O}_3$ | polystyrene | 8.5×10^{-38} |
| Ex. 11 | $\text{SiO}_2 \cdot \text{Al}_2\text{O}_3$ | polymethyl methacrylate | 4.8×10^{-40} |
| Ex. 12 | $\text{SiO}_2 \cdot \text{Al}_2\text{O}_3$ | n-butanol | 7.3×10^{-38} |
| Comp. Ex. 1 | $\text{SiO}_2 \cdot \text{Al}_2\text{O}_3$ | --- | |
| Comp. Ex. 2 | $\text{SiO}_2 \cdot \text{Al}_2\text{O}_3$ | monomethyl trimethoxysilane | 1.9×10^{-40} |
| Comp. Ex. 3 | $\text{SiO}_2 \cdot \text{ZrO}_2$ | --- | |

Table 1 (cont.)

| | Dispersion medium | | Stability I | |
|-------------|--------------------------|---------------------|-----------------------|-----------------------|
| | | dielectric constant | sulfuric acid | hydrochloric acid |
| Ex. 1 | ethylene glycol | 38 | stable at least 6 mo. | stable at least 6 mo. |
| Ex. 2 | ethylene glycol | 38 | stable at least 6 mo. | stable at least 6 mo. |
| Ex. 3 | ethylene glycol | 38 | stable at least 6 mo. | stable at least 6 mo. |
| Ex. 4 | ethylene glycol | 38 | stable at least 6 mo. | stable at least 6 mo. |
| Ex. 5 | N-methyl pyrrolidone | 32 | stable at least 6 mo. | stable at least 6 mo. |
| Ex. 6 | γ -butyro lactone | 39 | stable at least 6 mo. | stable at least 6 mo. |
| Ex. 7 | ethylene glycol | 38 | stable at least 6 mo. | stable at least 6 mo. |
| Ex. 8 | ethylene glycol | 38 | stable at least 6 mo. | stable at least 6 mo. |
| Ex. 9 | methyl cellosolve | 17 | stable at least 6 mo. | stable at least 6 mo. |
| Ex. 10 | ethylene glycol | 38 | stable at least 6 mo. | stable at least 6 mo. |
| Ex. 11 | ethylene glycol | 38 | stable at least 6 mo. | stable at least 6 mo. |
| Ex. 12 | ethylene glycol | 38 | stable at least 6 mo. | stable at least 6 mo. |
| Comp. Ex. 1 | ethylene glycol | 38 | visc. up 15 days | visc. up 20 days |
| Comp. Ex. 2 | ethylene glycol | 38 | gelled 30 days | gelled 40 days |
| Comp. Ex. 3 | N-methyl pyrrolidone | 32 | gelled 20 days | gelled 20 days |

Table 2

| | Sol composition | Modifying organic compound | mol. polarizability |
|-------------|--|------------------------------------|--------------------------|
| Ex. 1 | SiO ₂ ·Al ₂ O ₃ | γ-glycidoxypropyl trimethoxysilane | 10.4 x 10 ⁻⁴⁰ |
| Comp. Ex. 2 | SiO ₂ ·Al ₂ O ₃ | — | — |
| Ex. 13 | SiO ₂ | γ-glycidoxypropyl trimethoxysilane | 10.4 x 10 ⁻⁴⁰ |
| Comp. Ex. 4 | SiO ₂ | — | — |

Table 2 (cont.)

5

| | Dispersion medium | dielectric constant | Stability II (day) |
|-------------|-------------------|---------------------|--------------------|
| Ex. 1 | ethylene glycol | 38 | 62 |
| Comp. Ex. 1 | ethylene glycol | 38 | 4 |
| Ex. 13 | water | 77 | 43 |
| Comp. Ex. 4 | water | 77 | 2 |

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Table 3

| | Sol composition | Modifying organic compound | mol. polarizability |
|-------------|--|------------------------------------|--------------------------|
| Ex. 1 | SiO ₂ ·Al ₂ O ₃ | γ-glycidoxypropyl trimethoxysilane | 10.4 x 10 ⁻⁴⁰ |
| Comp. Ex. 1 | SiO ₂ ·Al ₂ O ₃ | - | - |
| Ex. 13 | SiO ₂ | γ-glycidoxypropyl trimethoxysilane | 10.4 x 10 ⁻⁴⁰ |
| Comp. Ex. 4 | SiO ₂ | - | - |

Table 3 (cont.)

5

| | Dispersion medium | dielectric constant | Stability III (day) |
|-------------|-------------------|---------------------|---------------------|
| Ex. 1 | ethylene glycol | 38 | 14 |
| Comp. Ex. 1 | ethylene glycol | 38 | 1 |
| Ex. 13 | water | 77 | 41 |
| Comp. Ex. 4 | water | 77 | 2 |

Table 4

| | Sol composition | Modifying organic compound | mol. polarizability |
|-------------|------------------|--|------------------------|
| Ex. 13 | SiO ₂ | γ -glycidoxypropyl trimethoxysilane | 10.4×10^{-40} |
| Comp. Ex. 4 | SiO ₂ | - | - |

Table 4 (cont.)

5

| | Dispersion medium | dielectric constant | Stability IV (min) |
|-------------|-------------------|---------------------|--------------------|
| Ex. 13 | water | 77 | 2880 |
| Comp. Ex. 4 | water | 77 | 60 |

Table 5

| | Sol composition | Modifying organic compound | mol. polarizability |
|-------------|------------------|--|------------------------|
| Ex. 13 | SiO ₂ | γ -glycidoxypropyl trimethoxysilane | 10.4×10^{-40} |
| Comp. Ex. 4 | SiO ₂ | - | - |

Table 5 (cont.)

10

| | Dispersion medium | dielectric constant | Stability V (day) |
|-------------|-------------------|---------------------|-------------------|
| Ex. 13 | water | 77 | 60 |
| Comp. Ex. 4 | water | 77 | 2 |

What is claimed is:

1. An inorganic compound sol comprising a dispersion medium and, dispersed therein, inorganic compound particulates whose surface has been modified by an organic compound exhibiting a molecular polarizability of from 2×10^{-40} to $850 \times 10^{-40} \text{ C}^2\text{m}^2\text{J}^{-1}$.

2. The inorganic compound sol as claimed in claim 1, wherein the inorganic compound particulates are silica particulates.

3. The inorganic compound sol as claimed in claim 1, wherein the inorganic compound particulates are composite oxide particulates composed of silica and at least one inorganic oxide other than silica.

4. The inorganic compound sol as claimed in claim 1, wherein the dispersion medium has a dielectric constant of from 10 to 85.

ABSTRACT

The inorganic compound sol of the present invention comprises a dispersion medium and, dispersed therein, inorganic compound particulates whose surface has been
5 modified by an organic compound exhibiting a molecular polarizability of from 2×10^{-40} to $850 \times 10^{-40} \text{ C}^2\text{m}^2\text{J}^{-1}$. This inorganic compound sol modified by an organic compound has desirable affinity with dispersion media, so that its dispersion stability in solvents is excellent without
10 aggregation of particulates.

Declaration and Power of Attorney For Patent Application

English Language Declaration

As a below named inventor, I hereby declare that:

My residence, post office address and citizenship are as stated below next to my name,

I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled

INORGANIC COMPOUND SOL MODIFIED BY ORGANIC COMPOUND

the specification of which

(check one)

☒ is attached hereto.

☐ was filed on _____ as

Application Serial No. _____

and was amended on _____
(if applicable)

I hereby state that I have reviewed and understand the contents of the above identified specification, including the claims, as amended by any amendment referred to above.

I acknowledge the duty to disclose information which is material to the examination of this application in accordance with Title 37, Code of Federal Regulations, §1.56(a).

I hereby claim foreign priority benefits under Title 35, United States Code, §119 of any foreign application(s) for patent or inventor's certificate listed below and have also identified below any foreign application for patent or inventor's certificate having a filing date before that of the application on which priority is claimed:

| Prior Foreign Application(s) | | | Priority Claimed | |
|------------------------------|-----------|------------------------|-------------------------------------|--------------------------|
| 57787/1997 | Japan | 12/March/1997 | <input checked="" type="checkbox"/> | <input type="checkbox"/> |
| (Number) | (Country) | (Day/Month/Year Filed) | Yes | No |
| _____ | _____ | _____ | <input type="checkbox"/> | <input type="checkbox"/> |
| (Number) | (Country) | (Day/Month/Year Filed) | Yes | No |
| _____ | _____ | _____ | <input type="checkbox"/> | <input type="checkbox"/> |
| (Number) | (Country) | (Day/Month/Year Filed) | Yes | No |

I hereby claim the benefit under Title 35, United States Code, §120 of any United States application(s) listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States application in the manner provided by the first paragraph of Title 35, United States Code, §112, I acknowledge the duty to disclose material information as defined in Title 37, Code of Federal Regulations, §1.56(a) which occurred between the filing date of the prior application and the national or PCT international filing date of this application:

| (Application Serial No.) | (Filing Date) | (Status) |
|--------------------------|---------------|--------------------------------|
| | | (patented, pending, abandoned) |

| (Application Serial No.) | (Filing Date) | (Status) |
|--------------------------|---------------|--------------------------------|
| | | (patented, pending, abandoned) |

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

POWER OF ATTORNEY: As a named inventor, I hereby appoint the following attorney(s) and/or agent(s) to prosecute this application and transact all business in the Patent and Trademark Office connected therewith. (list name and registration number)

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